The Influence of Inorganic Salts and Bases on the Formation of the J-band in the Absorption and Fluorescence Spectra of the Diluted Aqueous Solutions of TDBC

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We studied the influence of inorganic salts and bases on absorption and fluorescence spectra of diluted aqueous solutions of 5, 6-dichloro-2-[3-[5, 6-dichloro-1-ethyl-3-(3-sylfopropyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt (TDBC). Addition of inorganic salts or bases led to the appearance of an intense J-band and to the disappearance of monomer bands, even when the concentration of TDBC was as small as 2.3×10^{-8} mol/L. Salts and bases also significantly changed the maximal temperature at which the J-band was still observed in the spectra of the solutions. Finally, they affected the position of the maximum and the shape of the J-band.

I. Introduction

In 1936 Scheibe[1] and Jelley[2] reported that the absorption spectra of concentrated solutions of some cyanine dyes show a new, very narrow and intense band, red-shifted compared to the absorption spectrum of diluted solutions. This band was named the J-band in honor of E. E. Jelley. The band was attributed to the formation of a type of molecular aggregates, J-aggregates. Formation of large molecular aggregates in concentrated solutions of cyanine dyes was recently directly demonstrated.[3−4]

Since the pioneer papers of Scheibe and Jelley, enormous work has been performed with the purpose of establishing the nature of the J-band. The J-band was observed not only in solutions but also in glasses and films. It was found that J-aggregates have many unique optical properties, such as superradiant fluorescence,[5−11] nearly resonant with absorption, high second and third-order nonlinear susceptibility,[12−14] and optical activity.[15−17]

There are two published theories describing the nature of the J-band. Frank and Teller[18] suggested that the extremely strong and narrow J-band is due to the formation of an excitonic state through the electronic coupling of the tightly packed dye molecules in aggregates. This theory received development in numerous publications[19−26] and is accepted everywhere. Recently V. V. Egorov suggested another approach[27] to the nature of the J-band. According to his theory, the red shift of the J-band is caused by elongation of the dye chromospheres on aggregation. This is explained to be due to a $\pi-\pi$ electron interaction of the heterocyclic rings of neighbor molecules. The narrow shape of the J-band is attributed to an electron transfer and an unusual resonance between the electronic motion and environmental nuclear reorganization motion.

The excitonic theory predicts that the position of the maximum of the J-band and its width depend on the number of coupled chromophores; Egorov's theory conjectures that the number of molecules in the aggregate affects only the wings of the J-band. Both models assume that the formation of the J-band is caused by the aggregation of dye molecules; they do not assign a possible role to the solvent or glass.

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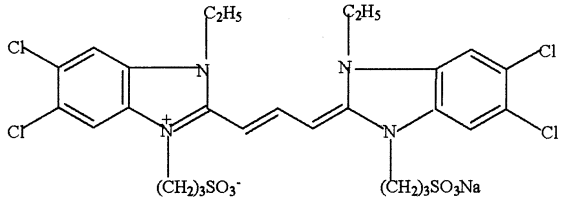

Figure 1. Structural formula of TDBC.

Many experiments on J-aggregates were conducted in solutions containing salts. It was noticed that the addition of salts decreased the critical concentration required for the appearance of the J-band in spectra.[13,28−29] Inorganic salts were said to increase the effective dielectric constant of the solvent, promoting the aggregation.[28]

We extend the study of the influence of inorganic salts and bases on the formation of J-band to extremely low concentrations. In this paper we report that inorganic salts and bases caused the appearance of the intense J-band and disappearance of a monomer band in the absorption and fluorescence spectra, even when the concentration of TDBC was as low as 2.3×10^{-8} mol/L. The position of the maximum, the half width at the full maximum (HWFM) of the J-band, and the kinetics of its growth depended on the type of the salt or base.

II. Experimental Details and Results

TDBC was bought from Hayashibara Biochemical Laboratories, Inc. and used without further purification. The chemical structure of TDBC is shown in Figure 1. The dye has a conjugated chain, a positively charged nitrogen atom at one end of the chain, and three other nitrogen atoms, each with a lone electron pair. TDBC is an inner salt and a sodium salt. While dissolved, it exists in solutions as $TDBC^-$ anions and Na^+ cations. The three nitrogen atoms with lone electron pairs allow the $TDBC^-$ anion to react with water, forming colorless $TDBC^- - H^+$ or $TDBC^- - 2H^+$ cations.[28] Due to protonation, absorption of TDBC even in neutral solutions is not full.[28] TDBC is easily soluble in distilled water and is well known to show a J-band in the absorption and fluorescence spectra. The threshold concentration of TDBC required for the appear-

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ance of the J-band at room temperature in distilled water is $\approx 10^{-5}$ mol/L.

Absorption spectra and kinetics were recorded with a Perkin-Elmer Lambda-12 UV−vis spectrometer. Fluorescence spectra were recorded with a Perkin-Elmer Lambda 50-B luminescence spectrometer. We used a VWR scientific thermometer 61220 with its probe inserted directly into the cell to measure the temperature of the solutions and an IQ-150 pH-meter to measure the pH.

1. Influence of Inorganic Salts and Bases on the Absorption and Fluorescence Spectra of Aqueous Solutions of TDBC of Concentration 10^{-7} mol/L and Lower. When concentration of TDBC was 10^{-7} mol/L and lower, the solutions did not show any noticeable absorption, even in a 5-cm thick cell. They did not show noticeable fluorescence either. Absence of absorption and fluorescence is, most likely, the result of hydrolysis of TDBC, which we mentioned above. When salts or bases were added to the solutions, initially an absorption with the maximum at 513 nm and a fluorescence with the maximum at 535 nm appeared. These are typical maxima of the absorption and fluorescence of TDBC monomers. Further addition of salts or bases caused the decrease of the absorption and fluorescence of monomers and the appearance of the J-band. Past a critical salt or base concentration, the absorption and fluorescence spectra showed the J-band and did not show significant absorption and fluorescence of TDBC monomers.

Figure 2 shows the influence of KOH on the absorption (2a) and fluorescence (2b) spectra of 2.3×10^{-8} mol/L water solution of TDBC. The spectra were measured at 25 °C. The overall absorption (area under the curve) in the 2.3×10^{-8} mol/L solution of TDBC was approximately the same at pH 9, 11, and 12 (spectra 1, 2, and 3 in Figure 2).

Addition of NaCl, KCl, Na_2SO_4, NaF, and NaOH had an effect on absorption and fluorescence spectra of highly diluted solutions of TDBC, similar to that shown in Figure 2. Figure 3 shows the influence of NaCl on absorption (3a) and fluorescence (3b) spectra of a 2.7×10^{-7} mol/L water solution of TDBC containing 0.001 mol/L of NaOH.

The position of the maximum and the HWFM of the J-band were slightly different in solutions containing different salts or bases. Thus, in solutions containing KOH and NaOH the maximum of the J-band in the absorption spectrum was at 593 nm. The maximum in the fluorescence spectrum was at 595 nm. In solution containing Na_2SO_4, the maximum of the J-band in the absorption spectrum was at 595 nm. The maximum in the fluorescence spectrum was at 597 nm.

2. Dependence of the Spectra and Kinetics of Moderately Concentrated Solutions of TDBC on the Type and Amount of Salt/Base. Figure 4 shows the absorption spectra of a 0.8×10^{-5} mol/L water solution of TDBC containing different amounts of sodium chloride measured at room temperature immediately after the addition of salts to the solution. Spectra were measured in a 1 cm cell. Three hours after preparation, the absorption spectrum of the 0.8×10^{-5} mol/L solution of TDBC in pure water at room temperature had only one maximum at 513 nm (curve 1, Figure 4). Addition of sodium chloride to the solution caused the disappearance of the absorption of monomers and the appearance of the J-band. The intensity of the J-band and the overall absorption initially increased with the increase of the amount of salt added (curves 2−5, Figure 4). However, starting from the concentration of 0.25 mol/L, further addition of NaCl did not lead to an increase of the intensity of the J-band and overall absorption.

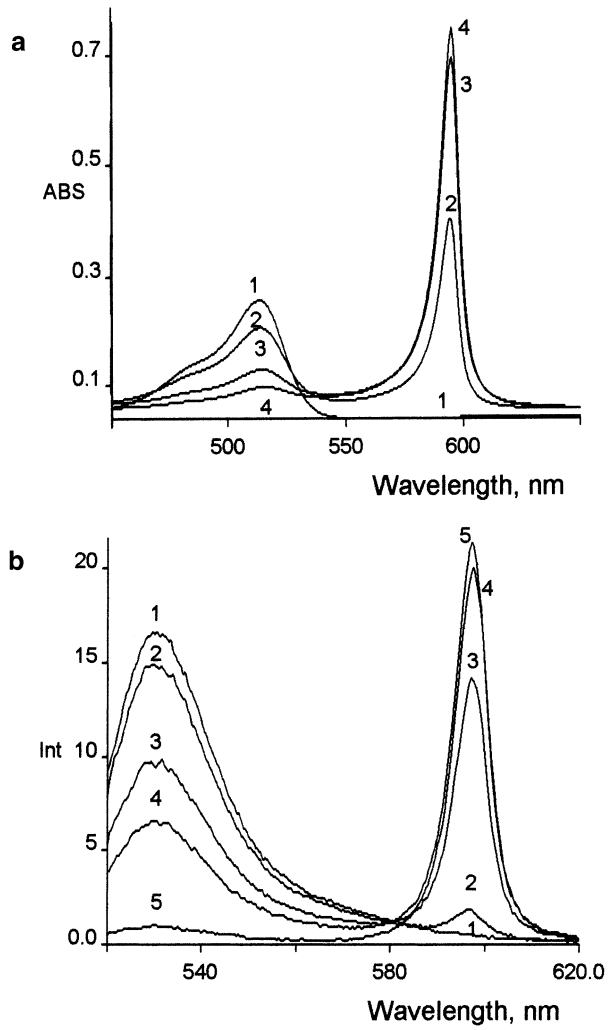

Figure 2. (a) Absorption spectra of 2.3×10^{-8} mol/L water solutions of TDBC containing different amounts of KOH. Optical path 5 cm. The pH of the solutions was 10.1(1), 11.8(2), 12.1(3), 12.5(4). (b) Fluorescence spectra of 2.3×10^{-8} mol/L solutions of TDBC containing different amounts of KOH. The pH of the solutions was: 10.1(1), 11.8-(2), 12.1(3), 12.5(4), 13.1(5). Excitation wavelength was 500 nm.

Addition of Na_2SO_4, $CaSO_4$, NaOH, and KOH to the solutions caused similar effects: the absorption with the maximum at 513 nm disappeared, the J-band appeared, and the intensity of the J-band and the overall absorption depended on the amount of salt/base. As in more diluted solutions, the position of the maximum and the HWFM of the J-band depended on the type of salt/base.

Addition of salts to more concentrated solutions of TDBC (10^{-4} mol/L and higher), showing an intense J-band in distilled water at room temperature, did not have a significant effect on the intensity of the J-band and overall absorption of the solutions. However, it prevented the decrease of the absorption of solutions taking place in the absence of salts.

Salts led to the increase of the temperature of the solutions, corresponding to the disappearance of the J-band. While in the absorption spectrum of a 3.0×10^{-5} mol/L solution of TDBC in distilled water the J-band completely disappeared at 60 °C, in the same solution containing NaCl it happened at 67 °C, and in solutions containing Na_2SO_4 and $CaSO_4$ only at 85 °C.

Salts significantly affected the kinetics of the formation of the J-band in water solutions of TDBC when the solutions were cooled from 90° C to room temperature. Figure 5 shows the kinetics of the absorption spectra of 3.0×10^{-5} mol/L solutions

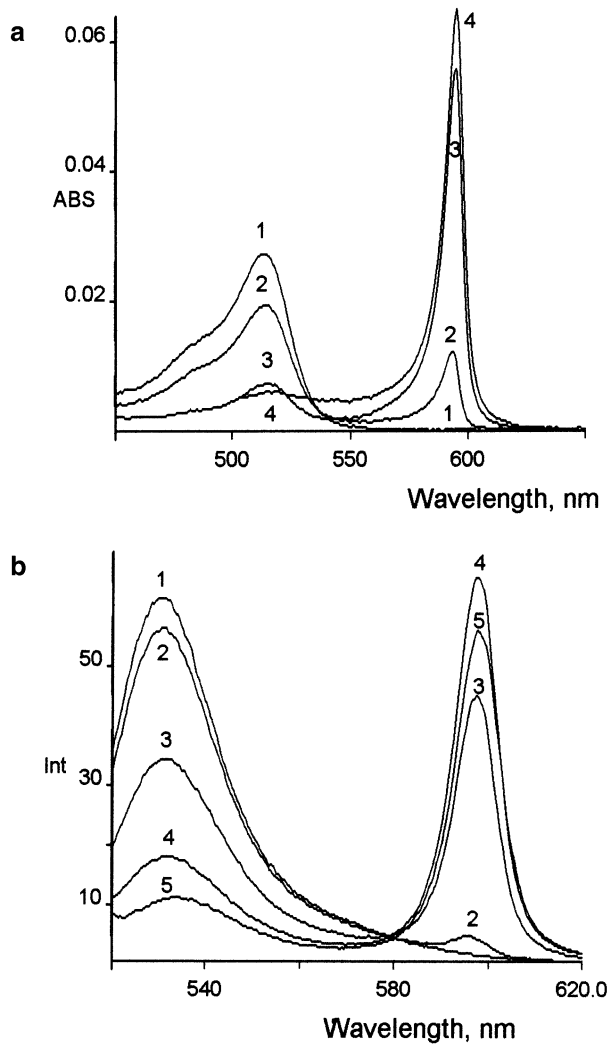

Figure 3. (a) Absorption spectra of 2.7×10^{-7} mol/L water solutions of TDBC containing 0.001 mol/L of NaOH and 0(1), 0.13(2), 0.34(3), and 0.89(4) mol/L of NaCl. Optical path 1 cm. (b) Fluorescence spectra of 2.7×10^{-7} mol/L solutions of TDBC containing 0.001 mol/L of NaOH and 0(1), 0.09(2), 0.34(3), and 0.89(5) mol/L of NaCl. Excitation wavelength was 500 nm.

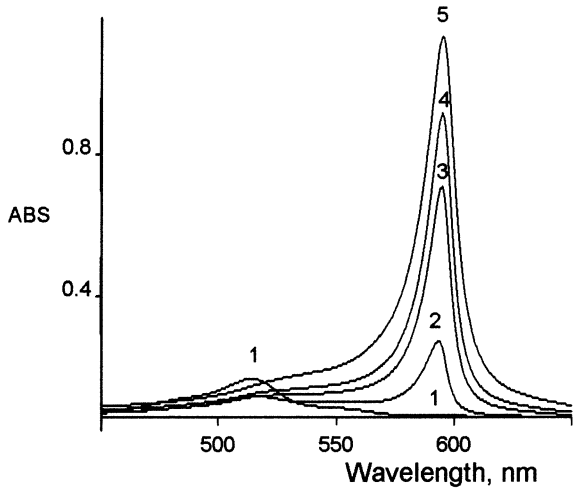

Figure 4. Absorption spectra of 0.8×10^{-5} mol/L solutions of TDBC containing 0(1), 0.07(2), 0.14 (3), 0.2(4), and 0.25(5) mol/L of NaCl.

of TDBC in distilled water (Figure 5a) and containing 0.005 mol/L of Na_2SO_4 (Figure 5b), measured with the time interval of 24 s between each spectrum. The J-band in the absorption

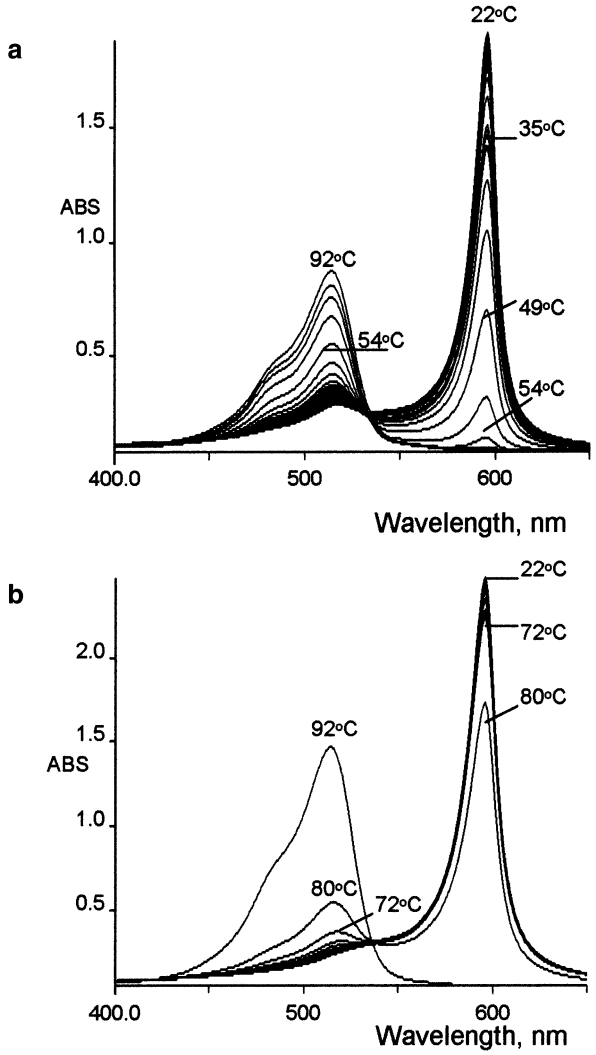

Figure 5. Kinetics of the absorption spectra of a 3.0×10^{-5} mol/L solution of TDBC in distilled water (a) and containing 0.005 mol/L of Na_2SO_4 (b) during their cooling from 90 °C to 22 °C. Time delay between spectra was 24 s.

spectrum of the solution of TDBC in pure water appeared approximately 144 s after the beginning of cooling, at temperature of 60 °C. The J-band in the absorption spectrum of the solution containing Na_2SO_4 appeared much sooner (24 s after the beginning of the cooling, at temperature 82 °C) and grew much faster. As it can be seen from Figure 5, no changes in the position of the maximum or in shape of the J-band in the process of its growth were observed.

III. Discussion

One of possible explanations of the influence of inorganic salts and bases on the J-band in the absorption spectra and kinetics of 10^{-5} mol/L solutions (Figures 4 and 5) may be catalysis of aggregation of cyanine dyes. Concentration of 10^{-5} mol/L corresponds to 6000 molecules per cubic micron. The size of a TDBC molecule is approximately 2 nm. It is possible that as a result of Brownian motion TDBC molecules approach each other and stick together. Inorganic ions may facilitate the formation of stable aggregates. First, inorganic salts increase the effective dielectric constant of water. This leads to less repulsion between $TDBC^-$ anions, facilitating their aggregation.[28] In addition, inorganic ions could shift the ionic balance in the solutions and thus promote aggregation/crystallization of TDBC.

The influence of salts and pH on the absorption spectra of highly diluted solutions of TDBC is not obvious. The appearance of the absorption belonging to monomers (at 513 nm) as a result of the increase of the pH (curves (1), Figures 2 and 3) could be explained by deprotonation of the $TDBC^- - H^+$ complex. It was mentioned in results that neutral salts (not just bases) added to highly diluted solutions of TDBC caused an initial recovery of the absorption of TDBC monomers. Therefore, neutral salts can somehow cause the deprotonation of the $TDBC^- - H^+$ complex. However, we are not sure how to explain the disappearance of the absorption of monomers and appearance of the intense J-band after further addition of salts or bases to 2.3×10^{-8} mol/L solutions of TDBC. Indeed, concentration of 10^{-8} mol/L corresponds to six molecules per cubic micron. Taking into account that the size of TDBC molecule is approximately 2 nm, one can visualize a 10^{-8}mol/L concentration as six 2-mm size particles per cubic meter. Even if inorganic salts or bases promote aggregation by reduction of the repulsion between $TDBC^-$ anions, it is unclear how TDBC molecules can approach each other in a short time in such conditions. Moreover, according to the published papers, mentioned in the Introduction, the number of molecules in aggregate required for the appearance of the J-band is at least three in the case of Egorov's theory and more than that in the case of excitonic theory. On the basis of the data presented in Figures 2 and 3, we have to assume that 99% of TDBC monomers in 10^{-8} mol/L solutions aggregated, forming at least three-molecular aggregates, leaving no monomers or dimers, and that they did it immediately after the addition of NaOH to the solutions. This seems very unlikely. In addition, we would like to point out that the spectra presented in Figures 2, 3b, and 5 show an isosbestic point. An isosbestic point usually indicates that the system exists in only two states.

Another experimental result that we are not sure how to explain is the difference in the behavior of the overall absorption after addition of salts or bases to highly diluted (2.3×10^{-8} mol/L) and moderately concentrated (10^{-5} mol/L) solutions of TDBC. We pointed out in the results section that in highly diluted solutions the addition of salts or bases initially caused the recovery of the absorption of monomers and then the formation of the J-band, without significant change of the overall absorption (Figure 2). In more concentrated solutions (Figure 4), salts (and bases) initially caused the decrease of the absorption of monomers and the appearance of the J-band and then the recovery of the overall absorption. One of the possible explanations of this difference is that in 10^{-5} mol/L solutions TDBC molecules partially exist in aggregates but do not show any absorption due to hydrolysis of aggregates. Addition of salts (or bases) initially catalyzes the aggregation of unprotonated $TDBC^-$ anions, leading to the appearance of the J-band and disappearance of the absorption of monomers. Further addition of the salts (or bases) leads to the deprotonation of TDBC molecules in aggregates and to the increase of the intensity of the J-band.

IV. Conclusion

Inorganic salts and bases have a very important influence on the absorption and fluorescence characteristics of water solutions of TDBC. The addition of salts and bases in significant amounts causes disappearance of the absorption and fluorescence of monomers and the appearance of the J-band in the spectra of highly diluted (10^{-8} mol/L) water solutions of TDBC. The intensity of the J-band depends on the amount and the nature of the salt (or base) added. More detailed research is required to draw conclusions on the nature of the influence of inorganic salts and bases on the J-band in the spectra of water solutions of TDBC. However, this influence is shown to be rather significant.

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